Project H-16: Structure and thermodynamic properties of complex hydrides

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This project is derived from HC-5. During 2002-2003 we concluded that the potential of carbon was limited for hydrogen storage, so finally decided to focus our IEA work exclusively on complex hydrides. In particular, we have initially focused on $LiBH_4$, with a contained H-content of 18.5 mass%. Using synchrotron XRD, we determined the room temperature crystal structure of $LiBH_4$ as orthorhombic Pnma (No. 62). There is a change in structure to tetragonal at about 105˚C, accompanied by a small release of H_2.

We have worked toward achieving reversible dehydriding/rehydriding behavior of $LiBH_4$, important for its use as an H-storage medium. The full reaction

$$LiBH_4 \leftarrow \rightarrow LiH + B + 3/2H_2$$

has the potential for 13.5 mass% H_2 storage, if it could be reversibly achieved at reasonable conditions. Of course, earlier work on $LiBH_4$ has shown this is not easy, especially the rehydriding (left arrow) reaction. The real question is whether it would be possible to catalyze H_2 desorption and reabsorption, as has been accomplished with $NaAlH_4$.

The figure summarizes some of the Fribourg temperature programmed desorption results, comparing uncatalyzed $LiBH_4$ with a SiO_2 catalyzed (25 mass%) sample. In both samples, three stages of desorption are observed. But the SiO_2 catalyst importantly lowers the onset temperatures for all three stages. For the uncatalyzed material, 9 mass% H_2 is evolved by 600˚C, whereas the catalyzed $LiBH_4$ released 12 mass% H_2 by 500˚C.

The rehydriding (left) reaction is more difficult to accomplish, but for the first time we have been able to directly reform $LiBH_4$ from LiH + B at 690˚C and 200 bar H_2 pressure.

The scientific understanding and practical utilization of catalyzed $LiBH_4$ is not yet understood and remains a challenge. Therefore, we will continue with our $LiBH_4$ work in 2004.

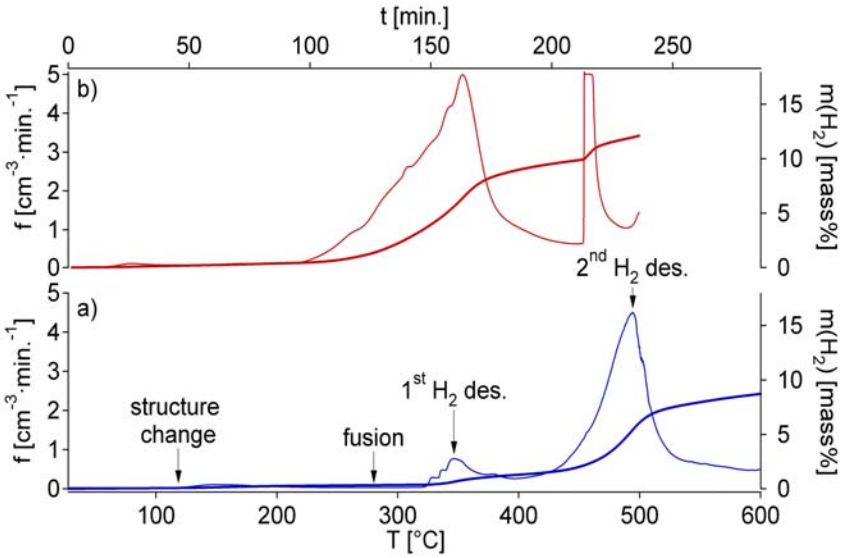

Figure – Effect of catalyst on thermal desorptiom spectra of $LiBH_4$. a) Uncatalyzed, b) SiO_2 catalyzed. Heating rate = 2 K min $^{-1}$. Light lines represent gas flow (left scale). Heavy lines represent integrated flow in mass% (right scale). [Züttel et al, J. Alloys Comp., 356-357 (2003) 515]